

BLM Letter of Mar 1, 2012

No QA Comments

Wyoming Water Development Office November 29, 2011

“An Explanation is needed of when and how did the apparent cross-contamination for some organic compounds in the water samples occur. Some organic compound detections in the sampling/trip blanks were at similar concentration to those levels also detected in some well water samples.”

During the April 2011 monitoring event, there was a USEPA Region 8 Laboratory irregularity in the reporting of ND (,50ug/L for Xylenes (total_ for sample EPAMW02-0411 (Method 8260B), when the summation of m,p-xylene (280 ug/L) and o-xylene (81.5ug/L should have been reported at 361.5 ug/L Xylenes (total) for this 04/19/11 sample.

During the April 2011 monitoring event, there was a USEPA Region 8 Laboratory irregularity in the reporting of ND (,50ug/L for Xylenes (total_ for sample EPAMW02D-0411 (Method 8260B), when the summation of m,p-xylene (354 ug/L) and o-xylene (102 ug/L should have been reported at 456 ug/L Xylenes (total) for this 04/19/11 sample.

2BE detected in only a few samples. Discrepancy?

Encana letter dated April 18, 2012

No QA comments

Encana Letter dated December 21

P2 - The EPA did not follow standard Quality Assurance Quality Control protocols when it drilled, completed, and sampled the two deep monitoring wells. The available evidence suggest that EPA may have backfilled the deep monitoring wells with drilling mud and drill cuttings. If true, the use of these materials could have potentially compromised the reliability of the deep monitoring data. In addition, the EPA detected seventeen compounds in “trip blanks” – QA/QC samples prepared using highly purified water – that were also found in the samples from the deep monitoring wells. As you know, the presence of these compounds in the “trip blanks” suggest that contaminants were introduced in the field and the laboratory, thereby impacting the reliability of the deep monitoring well samples. Overall serious questions remain concerning EPA’s QA/QC protocols.

Encana letter dated December 22

P3 – The EPA also reports that it detected tetraethylene glycol in QA/QC samples. QA/QC samples are used to assess whether contamination has been introduced during sampling or during analysis by the laboratory. These QA/QC samples are prepared using highly purified water. The presence of tetraethylene glycol in QA/QC samples casts significant doubt on the reliability of the EPA sample data collection process and demonstrates that the EPA introduced contamination in the field and the laboratory, thereby created the potential to impact the reliability of the groundwater samples. In total, the EPA detected seventeen compound in QA/QC samples.

P6 – The EPA did not use and adequate level of detail in the QA/QC and other sample protection procedures related to the level of analysis being conducted. The EPA has not provided the actual procedures used.

Review P 6 – While it is correct that the TPH measurements were not fractionated in accordance with current guidelines (e.g. EPA 2009b), numerous individual petroleum constituents of potential concerns were.... (2009b. Provisional Peer Reviewed Toxicity Values for Complex Mixtures of Aliphatic and Aromatic Hydrocarbons (CASRN Various). Prepared by Superfund Health Risk Technical Support Center, National Center for Environmental Assessment, Office of Research and Development, Final September 30, 2009)

Mike Mullen dated April 2012

No QA comments

Sterrett Report dated March 2012

RJS-12 – Molecules of gas will tend to migrate from high to low concentrations. Thus, that natural gas is present in the USEPA's groundwater monitoring wells is to be expected, as a result of natural processes that have occurred over millions of years, and are not related to gas development.

No QA comments

Halliburton / Environmental Resources Management (ERM) dated June 25, 2012

ES – 5 * US EPA utilized a non-standard analytical test method to analyze glycols and 2-butoxyethanol (2-BE), without validating the method and confirming that it was capable of producing reliable results (e.g., not prone to false positives). This unorthodox approach used by US EPA is reflected in the laboratory report narrative (US EPA Region III, 2011, emphasis added):

Because the method was being developed as samples were being analyzed, it is not known if the QC [quality control] data for percent recoveries and RPDs [relative percent differences] are appropriate."

The reliability of the glycols and 2-BE monitoring results are highly questionable, given the use of a non-standard and unproven analytical test method. This is an important deficiency because the Study places significant importance on the glycols and 2-BE data as "implicating" HF activities. The data quality limitations call the validity of this interpretation into serious question.

* A wide variety of compounds (e.g., hydrocarbons, methane, and glycols) were routinely detected in the field, equipment, and trip blank samples. For example, methane was detected in every blank sample (total of five) collected during Phase III and IV of the Study at concentrations ranging from 45 to 76 µg/L. No methane blanks were collected in Phases I and II. The routine and widespread detection of contaminants in the blanks is indicative of substandard field sampling practices. Finally, US EPA did not follow its own data quality assessment guidelines (e.g., US EPA, 2006) and did not take appropriate actions in addressing the presence of blank contamination. If US EPA had followed its own data quality assessment guidance (considering all concentrations less than 5 to 10 times the concentration detected in the blanks as non-detected), a large subset of the data for certain compounds, such as methane and hydrocarbons, would be considered non-detected.

Pg 18 - For the Pavillion project, US EPA did not follow its policy of generating data that are "scientifically valid,

defensible, and of known precision and accuracy." There were a number of data quality problems during the Study that demonstrate a lack of adequate planning (*e.g.*, choice of non-standard, unvalidated analytical test methods), poor field execution (*e.g.*, routine detection of contaminants in blanks), and disregard of US EPA guidance for assessing the usability of data for decision making (*e.g.*, the Study utilizes data that should have been qualified as non-detect due to the presence of contamination in the blanks), as discussed below.

*** Use of Non-Standard Analytical Test Method:** US EPA used a non-standard, unvalidated, analytical test method for conducting the analysis for glycols and 2-butoxyethanol (2-BE). Despite experiencing issues associated with false positives with glycols during the earlier phase of the Study (US EPA, 2011, p. 27), US EPA failed to undertake a method validation to evaluate whether "instrument" related interferences could cause false positives with the method it selected in Phase IV. This demonstrates lack of planning – a critical step in the US EPA-defined DQA process. The method was still "*under development*" (US EPA, 2011; emphasis added), when samples arrived at the laboratory. Consequently, there were a number of QA/QC problems during these analyses (*e.g.*, no surrogates were used, no QC criteria were pre-defined, retention times were not properly established). Overall, given the use of a non-standard, unvalidated, analytical method used by US EPA in Phase IV for conducting the glycol and 2-BE analysis, these data are of unknown quality, have not been shown to be reproducible, and, hence, should not be used for decision-making (see Section 4.2 for additional details).

*** Field Blank Contamination:** Field blanks provide an indication of contamination introduced during sample collection and handling and, consequently, are a critical component of a DQA program. During this Study, US EPA did not collect field blank samples consistently and/or did not use a uniform approach for applying blank-related "data qualifiers" (*e.g.*, when to consider a value detected *versus* non-detected) as part of the DQA process. For example, no blanks were collected for methane (in water) during Phases I and II, when a majority of the domestic well water methane data were collected. When US EPA collected methane blanks in Phases III and IV, all of the blanks exhibited methane contamination (23.0 to 76.4 µg/L), yet US EPA continued to use data collected in Phases I and II. These data are highly unreliable given that a majority of the domestic well water samples found methane concentrations comparable to the blanks (see Section 4.6).

Furthermore, during the Phase IV investigation, in addition to methane, benzene, toluene ethylbenzene, and xylenes (BTEX), gasoline range organic (GRO) hydrocarbons, DRO hydrocarbons, and glycols were found in a number of trip and field blanks (Table 3.2). The widespread detection of contaminants in the field blanks indicates that the field sampling program was not "in control." In addition, during Phases III and IV, US EPA used a blank-contamination evaluation that was not consistent with the approach used in Phase II (URS, 2010b) nor consistent with US EPA guidance (*e.g.*, US EPA, 1994). If US EPA had used a consistent approach, all concentrations less than the "Blank Action Level" presented below (Table 3.2) should have been qualified as non-detect as part of the DQA process. For example, all of the DRO concentrations in domestic wells were below the Blank Action Level and should be qualified as non-detect.

Table 3.2 Summary of Blank Contamination During Phases III and IV

Compound Detected in Blank	Maximum Blank Concentration (Source) (µg/L) ^a	Blank Action Level (µg/L) ^b	Comment
Phase III			
Methane (C1)	76.4 (field blank)	382 (5x)	Results below the blank action level would be considered non-detected ("U")
Toluene	0.54 (trip blank)	5.4 (10x)	
Phase IV			
DRO	135 (field blank)	675 (5x)	
Methane (C1)	45 (field blank)	225 (5x)	
Tetraethylene Glycol	3.6 (trip blank)	18.0 (5x)	
Toluene	0.228 (trip blank)	2.8 (10x)	
m&p Xylenes	0.229 (trip blank)	1.14 (5x)	

Notes:

(a) The maximum blank concentration is the highest concentration reported across all field, trip, or equipment blanks collected and analyzed during the indicated sampling Phase.

(b) Blank action levels are calculated as 5x the maximum blank concentration for most compounds and 10x for common laboratory contaminants such as toluene, methylene chloride, or bis(2-ethyl)hexylphthalate. The 5x and 10x blank action levels are consistent with Region VIII's July 27, 2010, memorandum "Treatment of Contamination Found in Method and Field Blanks for Pavillion Groundwater Investigation Sampling" (Parker, 2010). Results less than the indicated blank action level would be considered non-detected ("U").

(c) Field or trip blank data were not located for the Phase I investigation. During Phase II, although a field blank was collected for DRO and B270 analyses and a trip blank was collected for B260 and GRO analyses, field or trip blank data do not appear to be reported for methane analyses in water. DRO contamination was reported in the field blank collected during the Phase II investigation; however, US EPA Region 8 reviewed the data and determined there was no impact to the DRO results reported in the associated field samples.

Table 3.2 Summary of Blank Contamination During Phases III and IV

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Blank
Maximum Blank
Concentration (Source)
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**Blank Action Level
(µg/L)^b Comment**

Phase III

Methane (C1)

76.4 (field blank) 382 (5x)

Results below the blank action level
would be considered non-detected
("U")

Toluene 0.54 (trip blank) 5.4 (10x)

Phase IV

DRO 135 (field blank) 675 (5x)

Methane (C1) 45 (field blank) 225 (5x)

Tetraethylene

Glycol 3.6 (trip blank) 18.0 (5x)

Toluene 0.228 (trip blank) 2.8 (10x)

m&p Xylenes 0.229 (trip blank) 1.14 (5x)

Notes:

(a) The maximum blank concentration is the highest concentration reported across all field, trip, or equipment blanks collected and analyzed during the indicated sampling Phase.

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laboratory contaminants such as toluene, methylene chloride, or bis(2-ethyl)hexylphthalate. The 5x and 10x blank action levels

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considered non-detected ("U").

(c) Field or trip blank data were not located for the Phase I investigation. During Phase II, although a field blank was collected

for DRO and 8270 analyses and a trip blank was collected for 8260 and GRO analyses, field or trip blank data do not appear to

be reported for methane analyses in water. DRO contamination was reported in the field blank collected during the Phase II

investigation; however, US EPA Region 8 reviewed the data and determined there was no impact to the DRO results reported in

the associated field samples.

Pg 25 - The Reliability of Synthetic Organic Compounds Data Is Questionable

US EPA alleges that the presence of "synthetic organic compounds" (glycols, alcohols, and 2-BE) in the deep monitoring wells is an indication that HF fluids have affected the groundwater quality above the natural gas producing zone. US EPA states: "A wide variety of organic chemicals was detected in the monitoring wells including: GRO, DRO, BTEX, trimethylbenzenes, phenols, naphthalenes, acetone, isopropanol, tertiary butyl alcohol (TBA), 2-BE, 2-butanone, diethylene glycol, triethylene glycol, and tetraethylene glycol" (US EPA, 2011). However, the glycol and 2-BE data were generated using a nonstandard and unreliable test method and are not appropriate for use; all other constituents can be naturally occurring (see Section 4.3).

US EPA used a non-standard analytical test method to analyze groundwater samples collected from MW01 and MW02 to quantify concentrations for glycols (diethylene, triethylene, and tetraethylene) and 2-BE during Phase IV of the Study. The analyses were conducted using a LC/MS/MS method, which was not validated prior to use. It is well known that environmental measurements are not reliable unless the method used to produce the intended measurements has been adequately validated. For instance, the National Environmental Laboratory Accreditation Conference's (NELAC's) Quality System states for non-standard methods that "the method developed shall have been validated appropriately before use" (NELAC, 2002). According to the American Chemical Society, the "use of detailed testing to reveal sensitivity to interferences before adoption of a method is absolutely essential to ensure reliability" (ACS, 1980).

One of the key elements of method validation is to demonstrate that *false positives* are not being reported either due to instrument- or sample matrix-related interferences. When US EPA conducted glycol analyses at domestic wells, it could not replicate the results using two different methods and concluded that the detections were attributable to false positives due to "*interactions between the chromatographic column and organic compounds in sample water*" (US EPA, 2011, p. 27, emphasis added). Despite experiencing issues associated with false positives with glycols during the earlier phase of the Study, US EPA failed to undertake a method validation to evaluate whether instrument-related interferences could cause false positives with the method it selected in Phase IV. In addition, US EPA did not collect any field duplicates or matrix spike duplicates for glycol analyses, samples which would have helped in understanding whether the non-standard analytical method it chose in Phase IV was prone to problems (*i.e.*, interferences, false positives, or lack of precision) due to the complex sample matrix (*i.e.*, water sample saturated with methane, high pH, *etc.*).

Finally, some of the statements presented in the US EPA laboratory report narrative indicate that method development, QC, and analytical procedures were performed "on the fly" in the laboratory, which also severely affects the reliability of the glycol and 2-BE data (US EPA Region III, 2011):

"An appropriate surrogate has not yet been identified."

"Because the method was under development when samples arrived, a wide range of initial calibration standards were prepared."

"Because several quality control criteria (matrix spike/duplicate, CCV and SCV percent recoveries) were outside QC limits, all positive results should be considered estimated and have been qualified J."

"Because the method was being developed as samples were being analyzed, it is not known if the QC data for percent recoveries and RPDs are appropriate."

"Some blanks and samples...indicated very low levels of TeG in both the main and confirmation channel, but this may be the result of background noise or a coeluting interference."

These issues undermine the reliability of the glycol and 2-BE data for several reasons. For example, without appropriate surrogates, the potential effect of matrix interferences and false positives is not well understood. Furthermore, reliable chromatographic identification of target analytes requires establishing tight retention time windows for each analyte prior to performing field sample analyses. US EPA guidance recommends that to minimize this potential for false identifications, single component standards should be used for establishing retention times, stating "[b]efore establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions are optimized for the target analytes and surrogates in the sample matrix to be analyzed. Make three injections of all *single component standard mixtures* and multi-component analytes (such as PCBs) over the course of a 72-hour period" (US EPA, 2003, emphasis added). Apparently US EPA only used multicomponent standards to establish retention times, increasing the possibility of false positives. In addition, several QC parameters did not meet criteria, imposing uncertainty on data accuracy and precision, as well as method sensitivity.

As further evidence of the unreliability of the 2-BE data, only one of three labs that analyzed samples from MW01 and MW02 for 2-BE reported detectable results. Samples analyzed by US EPA Region III and the Kerr/Shaw laboratory (Kerr is part of the US EPA Office of Research and Development) did not report detectable 2-BE.

Overall, given the use of a non-standard, unvalidated analytical method used by US EPA in Phase IV for conducting the glycol and 2-BE analysis, these data are of unknown quality, have not been shown to be reproducible, and, hence, should not be used for decision-making.

Pg 27

One of US EPA's other lines of reasoning is that petroleum hydrocarbons (BTEX, trimethylbenzenes, naphthalene, GRO, and DRO) were detected in one or both of the deep monitoring wells (US EPA, 2011, p. 35). The detection of many constituents is questionable, however, given the contamination of field blanks (Sections 3.4 and 4.6). Thus, US EPA's data are not reliable for drawing conclusions about the presence or migration of contaminants. However, even if one assumes that the data are valid, the data would indicate that hydrocarbons found in the deep monitoring wells are consistent with those associated with natural gas, rather than providing evidence of hydraulic fracturing as suggested in the Study.

There was considerable variability noted in the BTEX and aromatic hydrocarbon content in the Pavillion condensate samples, despite there being limited variability in the light hydrocarbon gas composition (*i.e.*, all Pavillion natural gas samples have methane between 90 to 95%; Table A3b, US EPA, 2011). The variability in BTEX and aromatic hydrocarbon content is a symptom of the natural heterogeneity in the region and is consistent with the variability observed at MW01 and MW02.²⁴

²⁴ Low BTEX concentrations comparable to those measured in blanks were reported in MW01. These data should have been qualified as non-detects, consistent with US EPA data evaluation guidance (Parker, 2010).

Pg 28 - The distribution of DROs in domestic wells is consistent with the natural presence of hydrocarbons and heterogeneity in the study area or an artifact of the poor sampling practices utilized in the Study (see Section 3). If there were a contaminant source present at depth and contaminated groundwater was moving upward, then concentrations should exhibit an increasing trend with depth. However, the DRO concentrations do not increase with depth (Figure 4.2). It should also be emphasized that, due to DRO in QA (blank) samples, the DRO results for the drinking water samples are all below the Blank Action Level and should be considered nondetects (see Section 3.4).

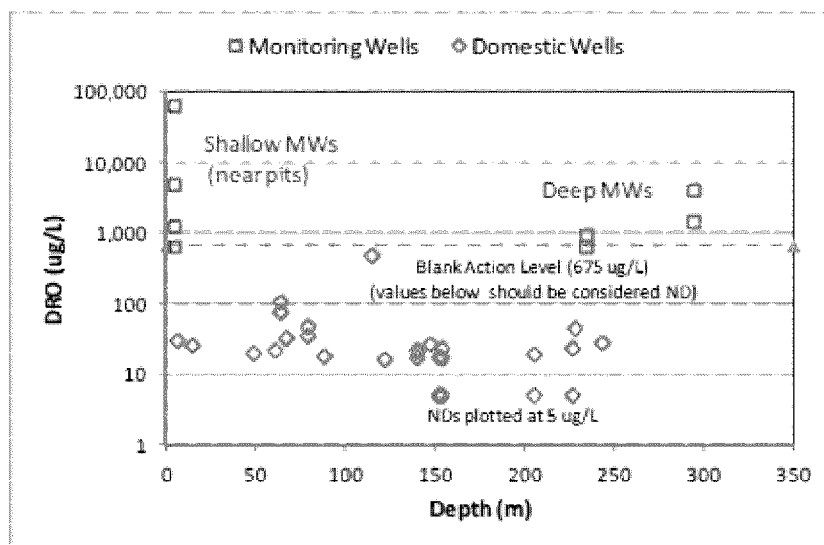


Figure 4.2 Concentrations of Diesel Range Organics (DRO) versus Depth

Pg 36 –

Figure 4.5 provides the maximum methane concentration in drinking water wells for the Pavillion study area, also depicting the locations of gas production wells. Taking the methane data at face value (*i.e.*, ignoring the blank contamination problems), there is no apparent spatial pattern in the methane data.

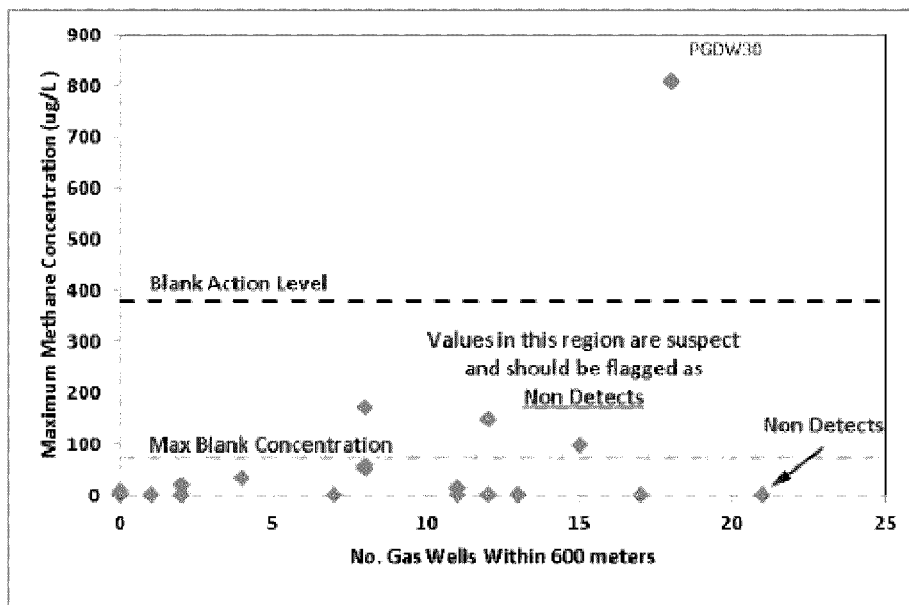


Figure 4.4 Methane in Drinking Water Wells as a Function of Proximity to Gas Wells

Pg 38 –

Of these wells, PGDW32 had no detectable methane in the Phase IV sampling, and only low levels in previous phases (21.4 µg/L in Phase I and 36.3 µg/L in Phase II). This draws into question whether methane is reliably present in this well, especially given the consistent detection of methane in blank samples. As discussed previously in Section 3.4 and in more detail below (in Section 4.6.4), the validity of the detected methane results for domestic wells is questionable given the pervasive methane contamination in field/trip blanks.

Pg 40 –

4.6.4 Methane Data Quality Problems Limit the Utility of the Data

The methane data have significant quality problems that severely affect the reliability of these measurements. In Phases III and IV of the Study, methane concentrations in field blanks were as high as 76.4 and 45 µg/L, respectively. This led US EPA to reject all Phase IV data where the sum of methane and ethane concentrations were less than 100 µg/L (US EPA, 2011, footnote on Table A3a). It is not clear why, despite the high detections in the corresponding blanks, US EPA did not reject any Phase III methane data. US EPA did not collect any methane blanks in Phases I and II, although given the consistent detections of methane in the Phase III and IV blanks, it is likely that Phase I and II data were also affected by blank contamination. Given these data quality problems, conclusions drawn from these unreliable methane data are likewise unreliable.

Pg 42

US EPA did not review the quality of the data adequately prior to utilizing the information for drawing conclusions and has therefore made statements that are overreaching and unsupported by the data. For example, US EPA used non-standard analytical test methods to analyze glycols and 2-BE without proper method validation, causing these results to be highly questionable. Additionally, a wide variety of compounds (e.g., hydrocarbons, methane, and glycols) were routinely detected in the field and trip blanks – an indication of sloppy field sampling practices. US EPA did not follow its own DQA guidance and did not take appropriate actions in addressing the presence of blank contamination. If it had, a large subset of the data for certain compounds, such as methane and hydrocarbons, would have been considered non-detects.

Sean Kelly dated March 8, 2012

Pg 12 –

7. Laboratory errors, contamination questions and non-repeatable laboratory results. There are several examples in the Draft Report where contamination is detected in blank control samples which are supposed to consist of pure distilled water. This is evidence of potential laboratory errors and/or contamination and raises additional questions about the validity and accuracy of all of the EPA data used in the study. The Draft Report also raises serious questions about the reliability and repeatability of the analytical methods used by the EPA to obtain the data which the study results are based upon.

- Some blank samples showed detections of acetone, m,p-xylene, toluene, benzoic acid and tetraethylene glycol (Draft Report Pg. 14). In at least three aquifer water samples reported in Draft Report Table 3 (Draft Report Pg. 24) levels of toluene, xylenes and tetraethylene glycol were detected at similar levels to the levels detected in blank control samples. These samples are identified by: "d Chemical detected in blank samples at a similar level". Where did this contamination come from?
- Elevated concentrations of diesel range organics were detected in one of six blank samples (Draft Report Pg. 14). Where did this contamination come from?
- In water samples collected from the two deep EPA monitor wells, one in eight samples had a detection of 2-Butoxyethanol (2-BE). In the well where 2-BE was detected, two of the three EPA labs conducting testing did not recognize 2-BE in duplicate samples. This raises suspicion of the EPA's ability to detect minute quantities of 2-BE, and the question: Was 2-BE actually present in any of the samples or is this simply a result of contamination? How can the EPA conclude that 2-BE is present based on this conflicting data?
- The EPA admits the need for "continued and future improvements of analytical methods to detect and quantitate low levels of organic chemicals that may be associated with hydraulic fracturing fluids" (Draft Report Pg. 27). This is in part due to unexplained inconsistencies in detecting glycols when comparing the results of gas chromatology combined with flame ionization to the results of liquid chromatology combined with mass spectroscopy. Evidently the gas chromatology combined with flame ionization (EPA Standard Method 8015) is prone to false positive results (Draft Report Pg. 27). Which of these methods was used to analyze for glycols the water samples obtained from the two deep EPA monitor wells during sampling phases III and IV? Was EPA Standard Method 8015 which is evidently prone to false positive results used to detect glycol concentrations in the monitor well water samples?
- The EPA apparently also used its own proprietary methods to analyze samples: "Detection of synthetic organic compounds was made in part through the use of non-commercially available modified EPA analytical methods (Draft Report Pg. 35)". Have these EPA methods and results ever been verified and confirmed for accuracy by any independent outside sources?

Papadopoulos and Associates dated April 26, 2012

Pg 11 =

2.4.2 Analysis of DRO and GRO

EPA's reporting of DRO and GRO results is problematic. GRO and DRO are multi-peak response mixtures containing hundreds of compounds, and the data reported do not provide sufficient information to interpret the data. There are a number of distinct issues associated with the DRO and GRO results. At the very least, EPA should perform a complete data validation on these results and provide appropriate data qualifiers to assist in interpretation. The key issues are as follows:

- Chromatograms for DRO and GRO results indicate that few of the samples show a good match with GRO and DRO standards, making the quantification of these results questionable;⁷
- Characteristic water-soluble compounds of gasoline and diesel (BTEX) are generally not present in the samples with GRO and DRO detections;
- BTEX compounds and DRO occur within a number of sample blanks at levels that would cause the results to be flagged as "non-detect" with appropriate data validation; and
- It is not clear if the GRO analyses were completed using acid-preserved or unpreserved

samples. Nor is it clear if the samples used for DRO analyses were subjected to silica gel column cleanup to remove potential biogenic interferences that may be present. If this cleanup is not completed, analyses of DRO often exhibit a high bias or are false positives. EPA does state on page 36 that "detection of gasoline range organics does not infer the use of gasoline for hydraulic fracturing." But, this limited statement misses the greater point that EPA has not identified what the organic chromatogram peaks in the DRO and GRO ranges actually represent. EPA has not eliminated the possibility that these are naturally occurring organic compounds. Consequently, the use of the phrases "diesel-range organics" and "gasoline-range organics" throughout the report is misleading, as it implies the presence of manufactured petroleum hydrocarbons, when that has not been demonstrated. EPA should provide all data required to recalculate the results reported. Advanced chemical fingerprinting (ACF) analytical methods should be considered to verify the absence and/or presence of petroleum hydrocarbon compounds.

7 EPA has not provided sufficient information to determine how quantification was achieved, and to determine the physical meaning of these results.

Pg 12

2.4.3 Gasoline Range Organics (GRO)

During Phases I and II, GRO was primarily detected in groundwater samples associated with the shallow monitoring wells at pits; concentrations in these wells ranged from hundreds to thousands of ug/L. GRO was detected in only three domestic wells (PGDW05, PGDW30, and PGDW32), at concentrations lower than 50 ug/L.

For all domestic wells, evaluation of chromatograms indicates a poor match to standard, and therefore a potentially erroneous quantification. In addition, GRO constituent compounds that should be detected in the volatile organic compound (VOC) analyses are widely not present in the domestic well samples. If GRO were present, then benzene, toluene, ethylbenzene and xylenes (BTEX) and other related petroleum hydrocarbon VOCs would be reported as detected in VOC analyses completed using gas chromatography/mass spectrometry (GC/MS).⁸ Consequently, the physical significance of the GRO results and their quantification are suspect in these domestic well samples.

In Phase III, TPH as gasoline was reported as detected in Sample MW01 at 389 ug/L. If GRO compounds were present, then BTEX and other gasoline-related components should have been detected in the VOC analyses by GC/MS. Only toluene, however, was detected (as a false positive) at a low concentration. Review of the corresponding VOC data shows that toluene was reported as detected in the field-, trip-, and equipment rinsate-blanks associated with this sample. Following data validation protocols, all toluene results at a concentration of ≤ 2.7 ug/L should be restated as undetected (U). Taking this into account, BTEX and other VOCs cannot be considered as detected in MW01 during Phase III, and the presence of GRO (as gasoline) is unlikely.

In Phase IV, TPH as gasoline was reported as detected in Sample MW01 at 592 ug/L. Review of the corresponding VOC data shows toluene and m, p-xylenes. In the two field blanks, however, m, p-xylene was also detected at 0.690 ug/L and 0.700 ug/L. After taking into account contribution of VOC due to blank contamination, only toluene would be considered as present in MW01 during Phase IV and there is no indication that GRO (as gasoline) is present.

The reported detection of TPH as gasoline in MW02 during the Phase III and IV investigations appears to be representative of a gasoline-range hydrocarbon compound and the chromatographic result is supported by the VOC by GC/MS results. A thorough review should be completed for all of the qualitative and quantitative data used by the laboratory for the TPH as gasoline analysis.

8 The relatively low reported concentrations of GRO could complicate such detections in some samples

2.4.4 Diesel Range Organics (DRO)

As with the GRO, the highest concentrations reported for DRO results were in the

shallow pit monitoring wells (up to 62,100 ug/L). Lower concentrations (mostly less than 100 ug/L) were reported for 18 domestic well samples and one municipal well sample.⁹ Intermediate concentrations were reported for the deep monitoring wells MW01 and MW02.

The quantification of DRO is suspect in most samples based on review of the sample chromatograms. There is a poor match to the diesel #2 standard used, and early eluting peaks not indicative of a diesel fuel product were primarily used for both qualitative and quantitative purposes.¹⁰ There is also a lack of agreement to other supporting data (e.g., analyses for semivolatile organic compounds (SVOCs) using GC/MS). The results also likely exhibit a high bias due to inclusion of non-petroleum related compounds (such as unidentified chromatographic peaks and plant waxes of likely terrigenous origin). Because of the poor match to standard, and insufficient supporting data to understand how these results were quantified, these DRO results provide only qualitative information. It is likely that many of the low detections of DRO reported for the domestic wells in the Phase II investigation represent false positive values. While a fuel product may be present in the Phase II samples, DRO was also reported as detected in the associated field blank at 26.5 ug/L. Therefore if these data were validated following guidance specified USEPA functional guidelines (U.S. EPA 2008), the results reported for PGMW01, PGMW02, and PGMW03 would be restated as undetected (U) because the concentrations prior to adjustment of the dilution factors were ≤ 5 times the concentration found in the field blank.

DRO was reported as detected in MW01 at 634 ug/L during the Phase III investigation and at 924 ug/L during the Phase IV investigation. For MW02 in the Phase III investigation, DRO was reported as detected at 1,440 ug/L and in the Phase IV investigation at 4,050 ug/L (and 4,200 ug/L in the duplicate sample). The DRO (as a petroleum product) detections are suspect in these samples because there is a poor match with the diesel #2 standard and there were many early eluting peaks that are not indicative of a diesel-range fuel product that were used for both qualitative and quantitative purposes. There were a few chromatographic peaks within the applicable carbon range, but the fingerprint did not appear to be that of an unweathered or weathered diesel fuel product.

⁹ Reported DRO results exceeded 100 ug/l for four of the domestic well samples. In all of these wells, DRO concentrations were, however, substantially lower in other samples. For example, concentrations dropped by more than 50% from Phase II to Phase IV for PGDW41 (479 to 132 ug/L) and for PGDW49 (130 to 59.1 ug/L). The reported concentration in PGDW22 varied from 27.1 ug/L in Phase I to 154 ug/L in Phase II.

¹⁰ The chromatogram for Sample PGDW30, however, may be representative of mineral spirits, stoddard solvent, or other similar type petroleum hydrocarbon; the laboratory annotated this chromatogram with the phrase "early diesel?". Residual range oil product eluting after the DRO range may possibly be present in some samples (e.g., PGDW05). The chromatograms of other samples (e.g., the trap sample) are indicative of alkanes representative of plant waxes of likely terrigenous origin.

2.4.5 Analysis of Glycol

EPA's reporting of glycol detections in domestic wells is misleading. On page 27 of the Draft Report, EPA states that the detection of glycols in several samples analyzed using a GC/FID technique (e.g. SW-846 Method) were likely reported as false positives. The Agency further states the glycol detections could not be confirmed using a liquid chromatography with tandem mass spectroscopy analysis.¹¹ It is well established that analysis by MS/MS is a significantly more accurate analytical technique and subject to fewer interferences than a GC/FID analytical method. As such, the confirmatory non-detected results should be used for interpretative purposes and not the GC/FID results for the domestic wells.

In contrast, the glycol analyses for the deep monitoring wells conducted during Phase IV (by HPLC/MS/MS) appear to be acceptable and these data are of generally good quality. These data tentatively indicate that glycol target compounds are present in MW01 and MW02. These analyses were, however, completed using a non-peer reviewed method on samples that may have been compromised by contact with cement during purging/sampling (see Section 2.3).

It is important to note that glycols (including diethylene glycol) are components of widely used cement grinding aids that contribute to the fluidity of crushed cement powder

(Ervanne and Hakanen, 2007; Grace Construction Products, pers. comm., 2012; Maslow, 1974; Strolman, 2002).¹² Experiments on glycol-containing admixtures suggest that such compounds are mobile in aqueous solutions in contact with cement (Herterich et al., 2003). Consequently, the presence of glycols in the deep aquifer, rather than as an artifact of poor well construction, should be confirmed through additional sampling and analysis.

¹¹ Referenced as GC/MS/MS in the report text.

¹² Glycols are also used in cement admixtures such as superplasticizers. The source of cement used to build wells MW01 and MW02 is not specified in EPA's field notes.

2.4.6 Other Qualified Data

EPA consistently uses qualified data in its interpretations, without addressing the significance of this qualification. This includes the use of sample results that should have been reported as non-detect due to blank contamination. Ultimately, this is a failure to use appropriate data validation. For example, there were detections of several target compounds (2-butanone, acetone, toluene) in blank water samples (method blanks, trip blanks, field blanks, and equipment rinsate blanks), and if the data were subjected to an appropriate degree of data validation, many results reported as detected would be restated as undetected (U) because the concentrations found in the samples were ≤ 5 times or ≤ 10 times the concentrations found in the associated blanks. (In laboratory data validation, a ratio of ≤ 5 is typically applied to uncommon contaminants, whereas a ratio of ≤ 10 is used for common contaminants such as acetone for VOC analyses and phthalate compounds for SVOC analyses.) The affected results would then either be restated as undetected (U) at the concentration found in the associated blank or at the concentration reported in the samples. Specific examples are provided in Appendix B.

EPA also acknowledges that several of the analytical method standard operating procedures (SOPs) that were used to complete chemical analyses were not official EPA methods, nor were they subject to required peer review (U.S. EPA, 2000a, 2002a). While the applicable methods may be capable of generating acceptable data, the use of non-EPA approved methods, coupled with the lack of appropriate (and required) peer review, may possibly bias or invalidate the affected data until they are subjected to a thorough review and are used by outside analytical laboratories. If a laboratory uses a nonstandard or unapproved method, EPA requires the data user to “provide method validation data to confirm that it will be adequate for the intended use of the data” (U.S. EPA, 2002b). Information that should be reported with the data would include “determination of detection limits, quantitation limits, typical recoveries, and analytical precision and bias” (U.S. EPA, 2002b). The evaluation of such data will “indicate the laboratory’s ability to demonstrate control of the method and document the quality of the data obtained” (U.S. EPA, 2002b).

EPA also conducted an incomplete and undocumented analysis of monitoring well drilling fluid additives, and then used the results to contend that the additives were not impacting water quality in MW01 and MW02. For example, there are two unknown samples (i.e., PAV1, and PAV2) from the drilling additives study conducted after well completion (July 2011; see *SampleResults_80A778SF_SS6163_23993_07-21-11_Headspace.pdf*). These samples are not described in the report, but have high concentrations of some organic compounds (TBA, alcohols, benzene, toluene) that EPA attributes to hydraulic fracturing fluids. In addition, EPA only conducted selected analyses on additive samples (Draft Report, Table 2). Chemical characterization of the dense soda ash, Quik Gel, and Quik-Trol Gold were not completed because “dissolved organic concentrations were low...” Nonetheless, analyses of the dense soda ash, Quik Gel, and Quik-Trol Gold should have been completed for all target organic compounds and all additives should have been analyzed for SVOCs, GRO, and DRO.

Pg 18 - As discussed above, there were also detections of several target compounds in many of the associated blank water samples (e.g., method blanks, trip blanks, field blanks, and equipment rinsate banks), and if the data were subjected to an appropriate degree of data validation, many results reported as detected would be restated as undetected (U).

pg 18 - There are also several issues related to the purported identification of isopropanol, tertbutyl alcohol, and other alcohol compounds in MW01 and MW02. These include the following:

- EPA acknowledges that several analytical method standard operating procedures (SOPs) that were used to complete some chemical analyses were not official EPA methods nor were they subject to required peer review (U.S. EPA, 2000a, 2002a);

pg 23 –

Detection of glycols in domestic well samples analyzed using a gas chromatography/flame ionization (GC/FID) technique, could not be confirmed with more accurate techniques, and therefore, should have been reported as non-detect for interpretive purposes. Detection of glycols in deep monitoring wells appears reliable, but requires additional confirmation due to the untested nature of the analytical methods and the potential impact of contact with cement phases (including glycol-bearing additives).

Table 1

Table 1 Organic Compounds Reported in Domestic (PGDW) Wells *

Analyte Comment Issues

1 1,1,2-Trichloro-1,2,2-trifluoroethane Chlorofluorocarbon,"detected"in"a"single"well Unrelated"to"HF

2 1,3-Dimethyladamantane

This"compound"was"detected"(with"qualification)"in" concentrations"up"to"1.81"ug/l""at"3"locations"in"Phase"II."

All"follow-up"samples"in"Phase"IV"were"similarly" qualified.""1,3-dimethyladamantane"was"also"

tentatively"identified"in"at"least"one"blank"sample" (Sample"1104026104"(trip"blank))"at"1.69"ug/l,""a"

concentration"higher"than"those"in"the"Phase"IV" domestic"wells"samples"(see"page"147"of"the"Phase"IV" laboratory"document).

Detections"are"not"confirmed

3 2,4,5-Trichlorophenol

Qualified"detection"in"1"well"in"Phase"II,"no"confirmation" in"later"Phases

Detections"are"not"confirmed

4 2,6-Dinitrotoluene

Qualified"detection"in"1"well"in"Phase"II,"no"confirmation" in"later"Phases

Detections"are"not"confirmed

5 2-Chlorophenol

Qualified"detection"in"2"wells"in"Phase"II,"no" confirmation"in"later"Phases

Detections"are"not"confirmed

6 2-Methylnaphthalene

Qualified"detections"in"Phase"II,"but"all"Phase"IV"results" were"ND

Detections"are"not"confirmed

7 4-Chloro-3-methylphenol

Qualified"detections"in"3"wells"in"Phase"II,"but"all"Phase" IV"results"were"ND

Detections"are"not"confirmed

8 Acenaphthene

Qualified"detections"in"2"wells"in"Phase"II,"but"all"Phase" IV"results"were"ND

Detections"are"not"confirmed

9 Acenaphthylene

Qualified"detrections"in"1"well"in"Phase"II,"but"all"Phase"
IV"results"were"ND
Detections"are"not"confirmed
10 Acetate One"detection"in"Phase"IV"at"0.102"ug/l
Multiple"possible"sources"from"degradation"of"organic"
matter
11 Adamantane
Qualified"detrections"in"Phase"II;"a"single"detection"in"
Phase"IV,"but"also"apcpared"in"Phase"III"equipment"
blank
Detections"are"not"confirmed
12 Aroclor!1016 One"detection"in"Phase"II,"but"no"Phase"IV"follow!up
Detections"are"not"confirmed;"Unrelated"to"HF
13 Benzene One"detection"in"Phase"II,"flagged"as"J"value Detection"not"confirmed
14 Bis(2!ethylhexyl)phthalate
Detections"in"Phases"I,"II"and"IV;"Most"phase"I"and"II"
results"qualified;"compounds"occurs"in"Phase"IV"trip"
blank"at"concentration"higher"than"most"detections
Detections"are"not"confirmed
15 Bis!(2!Ethylhexyl)"Adipate One"detection"in"Phase"IV"at"1.64"ug/l Detections"are"not"confirmed
16 Butanes Several"detections"in"Phase"II Multiple"possible"sources
17 Butyl"benzyl"phthalate
Qualified"detrections"in"Phase"II,"but"all"Phase"IV"results"
were"ND
Detections"are"not"confirmed;"Unrelated"to"HF
18 Caprolactam
Qualified"Detrections"in"Phase"I"and""II,"but"no"Phase"IV"
follow!up
Detections"are"not"confirmed;"Unrelated"to"HF
19 Chloroform
One"detection"in"Phase"II,"but"all"Phase"IV"results"were"
ND
Detections"are"not"confirmed;"Unrelated"to"HF
20 Chloromethane
Qualified"detrections"in"Phase"II,"but"all"Phase"IV"results"
were"ND
Detections"are"not"confirmed;"Unrelated"to"HF
21 Dimethylphthalate
Qualified"detrections"in"Phase"I,"but"all"Phase"IV"results"
were"ND
Detections"are"not"confirmed;"Unrelated"to"HF
22 Di!n!butyl"phthalate
Qualified"detrections"in"Phase"II,"but"all"Phase"IV"results"
were"ND
Detections"are"not"confirmed;"Unrelated"to"HF
23 Di!n!octyl"phthalate
One"Qualified"detrections"in"Phase"II,"but"all"Phase"IV"
results"were"ND
Detections"are"not"confirmed;"Unrelated"to"HF
24 Fluorene
Qualified"detrections"in"Phase"II,"but"all"Phase"IV"results"
were"ND
Detections"are"not"confirmed
25 Formate One"detection"in"Phase"IV
Multiple"possible"sources"from"degradation"of"organic"

Matter

26 Heptanes Detections "in" Phase "II," but "no" follow!up Multiple "possible" sources

27 Hexanes Detections "in" Phase "II," but "no" follow!up Multiple "possible" sources

28 Methylene chloride

One "detection" in "Phase" II, "but" all "Phase" IV "results" were

ND

Detections "are" not "confirmed;" Unrelated "to" HF

29 Naphthalene

Qualified "detections" in "Phase" II, "but" all "Phase" IV "results"

were "ND

Detections "are" not "confirmed;" multiple "possible" sources

30 Octanes Detections "in" Phase "II," but "no" follow!up Detections "are" not "confirmed;" multiple "possible" sources

31 Pentanes Detections "in" Phase "II," but "no" follow!up Detections "are" not "confirmed;" multiple "possible" sources

32 Phenol

Qualified "detections" in "Phase" II, "but" all "Phase" IV "results"

were "ND

Detections "are" not "confirmed;" multiple "possible" sources

33 Propanes

One "detection" in "Phase" II, "but" all "Phase" IV "results" were

ND

Detections "are" not "confirmed

34 Styrene

One "detection" in "Phase" II, "but" all "Phase" IV "results" were

ND

Detections "are" not "confirmed

35 Tetrachylene Glycol All "results" are "qualified!" "see" text Detections "are" not "confirmed

36 Toluene Detections "in" Phase "II" and "IV Multiple "possible" sources

37 Triethylene Glycol All "results" are "qualified!" "see" text Detections "are" not "confirmed

38 Tris "(2!butoxyethyl)" phosphate

Qualified "detections" in "Phase" II, "but" all "Phase" IV "results"

were "ND

Detections "are" not "confirmed

QA/QC Solutions for Papadopoulos dated February 22, 2012

Pg 1 -

1. All data reported by USEPA should be subjected to a thorough internal and independent thirdparty

data verification, data validation, data quality assessment (DQA), and data usability evaluation prior to its use. Completion of these tasks will allow for a better understanding of the overall quality of the data; verify that all applicable QA/QC procedures were documented and completed; identify potential limitations (if any) of the data; and, to help determine, with a known degree of confidence, if the data are usable for their intended purpose(s). A brief summary of some of the elements regarding QA/QC processes and procedures, data verification, data validation, DQA, and data usability evaluation are provided in Attachment 1 for reference.

3. Complete documentation of all data collected during the investigation is not yet fully posted on the USEPA website. Until such time that all analytical data is made available, a thorough assessment of the overall quality of the data cannot be completed at this time.

4. The USEPA acknowledges that several of the analytical method standard operating procedures

(SOPs) used to complete some chemical analyses are not official EPA approved methods nor were they subjected to the required peer review (U.S. EPA 2000, 2002a); see note below.

These

SOPs are probably capable of generating acceptable and repeatable data; however, the use of non-

EPA approved methods, coupled with the lack of appropriate (and required) peer review, could possibly result in the reporting of potentially biased data. It should be noted, however, that the USEPA reported applicable QC measurement data that included method blanks, surrogate compound recoveries, matrix spike and matrix spike duplicate recoveries, results of standard reference material (SRM) analyses, and laboratory duplicate sample analyses. The results of these

QC measurements were generally acceptable, indicating the methods used for analysis are capable of producing data of good quality. In addition, the USEPA should state why these SOPs have not been subjected to the peer review process.

5. There is not sufficient information available to completely address the qualitative and quantitative

concerns regarding the GRO and DRO analytical results reported. A detailed description of how the USEPA is defining, qualitatively identifying, and quantifying GRO and DRO should be provided. The data currently available does not permit an independent verification of the GRO and DRO: complete quantification lists are not provided that list all of the chromatographic peaks

that were used for qualitative purposes and the area or peak counts of those chromatographic peaks that were summed for quantitative purposes. Without this information it is not possible to determine what chromatographic peaks were used for qualitative and quantitative purposes and the validity of the data reported.

SW-846 Method 8015D (U.S. EPA 2011b) defines GRO as the range of alkanes from C6 to C10 and DRO as the range of alkanes from C10 to C28. The sum of the peak areas (or peak height if used) of all applicable chromatographic peaks eluting within these specified carbon ranges are used for quantitative purposes. The GRO and DRO analytical methods will result in the detection of many nonalkane and non-petroleum based compounds. Depending on the qualitative and quantitative criteria that were used, GRO or DRO then may be reported as a false positive or biased high because other compounds that may be present, such as naturally occurring organics, that elute within the applicable carbon ranges.

7. It was not evident in the data made available for review if the GRO analyses were completed using acid preserved to pH <2 samples or were they unpreserved. This should be clarified.

9. The presence of GRO (i.e., TPH as gasoline) is suspect in most samples, but appears to be present

in a few samples. The determination that the presence of GRO is suspect is based on the findings

there is a poor match of the sample chromatogram to the standard used for qualitative purposes and that common constituents found in gasoline (e.g., BTEX and additives such as MTBE) were not detected or were present at very a low concentration and not confirmed in the VOC analyses completed using gas chromatography/mass spectrometry (GC/MS) using SW-846 Method 8260B

(U.S. EPA 2011b). For those samples in which the presence of TPH as gasoline is plausible, its presence is supported by the detection of BTEX and other additives by the GC/MS method; however, the results reported for TPH as gasoline likely exhibit a high bias due to inclusion of non-petroleum related compounds as a result of the general requirements specified by the

method

and briefly discussed above. A few examples to illustrate the comments above include the following:

! For Phase I, data summaries and original instrument printouts for the GRO and VOC analyses were posted on the USEPA website.

! For Phase II, no field blank data (e.g., trip blanks or field blanks) were reported along with the sample results. The highest concentrations of TPH as gasoline were reported in samples PGMW01 at 389 ug/L, PGMW01D at 322 ug/L, PGMW 2,210 ug/L, and PGMW03 at 1,060 ug/L. The corresponding VOC results by GC/MS using SW-846 Method 8260B (U.S. EPA 2011b) for these samples typically reported as detected benzene, ethylbenzene, and xylenes, 1,3,5-Trimethylbenzene, tert-Butylbenzene, adamantane, and 1,3-Dimethyl adamantane; toluene was either not detected or was present at a very low concentration. The concentration of benzene was atypically elevated compared to the other aromatic VOCs, which does indicate the presence of an unweathered or weathered gasoline profile. Further data analysis is recommended.

! TPH as gasoline was reported as detected in Sample MW01 in the Phase III investigation at 389 ug/L. BTEX (and other gasoline-related components) should be detected in the VOC analyses by GC/MS using SW-846 Method 8260B (U.S. EPA 2011b); however, only toluene was detected (as a false positive) at a very low concentration. Review of the corresponding VOC data shows that toluene was reported as detected at 0.750 ug/L in MW01 and was also detected at 0.160 ug/L in the field blank, 0.540 ug/L in the trip blank, and 0.160 ug/L in the equipment rinsate blank associated with this sample.

In following data validation protocols using the !5 times rule for uncommon contaminants by using the highest concentration found in any blank and taking into account any dilution factors (U.S. EPA 2008), all toluene results

reported as detected at a concentration of !2.7 ug/L in all samples associated with this trip blank should be restated as undetected (U) at the concentration reported (if greater than that found in the blank) or restated as undetected at the concentration found in the blank if the concentration in the sample was lower. VOCs were not reported as detected in the method blank.

After taking into account contribution of VOC due to blank contamination, it is evident that BTEX and other VOCs are not present in MW01 during Phase III and the presence of GRO (as gasoline) is unlikely. This type of example is found with several other samples.

! TPH as gasoline was reported as detected in Sample MW01 in the Phase IV investigation at 592 ug/L. BTEX (and other gasoline-related components) should be detected in the VOC analyses by GC/MS using SW-846 Method 8260B). Review of the corresponding VOC data shows that toluene at 0.560 ug/L, m,p-xylenes at 0.890 ug/L, 2-Hexanone at 0.370 ug/L, 4-methyl-2-pentanone at 2.60 ug/L, and acetone at 79.5 ug/L were reported as detected in MW01. In the two field blanks, m,p-xylene was detected at 0.690 ug/L and 0.700 ug/L, in addition to 2-Butanone at 0.640 ug/L and 0.820 ug/L, 2-Hexanone at 0.290 ug/L and 0.410 ug/L, acetone at 1.03 ug/L and 1.38 ug/L, and methacrylonitrile at 0.270 ug/L and not detected in second field blank. Chloromethane was the only VOC reported as detected in the trip blank at 1.04 ug/L. VOCs were not reported as detected in the method blank. Using the !5 times rule for uncommon contaminants and the !10 times rule

for common contaminants with highest concentration found in any blank and taking into account any dilution factors (U.S. EPA 2008), the toluene results are considered acceptable because this VOC was not detected in the associated blanks. However, all associated samples results would be restated as undetected if the concentration was 13.5 ug/L for m,p-xylene, 12-Butanone at 14.1 ug/L, 2-Hexanone at 1.05 ug/L, and acetone at 13.8 ug/L. After taking into account contribution of VOC due to blank contamination, only toluene would be considered at present in MW01 during Phase IV and there is no indication that GRO (as gasoline) is present.

The reported detection of TPH as gasoline in MW02 during the Phase III and IV investigations appears to be representative of gasoline and supported by the VOC by GC/MS results.

10. At this time there is no indication if any of the samples analyzed for DRO were subjected to silica

gel column cleanup (or any other cleanup procedures) for the analysis of DRO. Cleanup of sample extracts is often necessary to remove or minimize interferences caused by non-target analytes that may be present so that more reliable qualitative identification and more accurate quantification can be completed. Silica gel retains the polar, naturally occurring, compounds while the non-polar, petroleum-based hydrocarbons remain in the extract. Use of this cleanup allows for more reliable qualitative identification and quantification to minimize the reporting of potential positive or biased high data (e.g., reporting of concentrations that are actually lower than are quantified). Additional cleanup procedures, such as alumina, may also be used to further

minimize non-target analyte interferences. The USEPA should state if the samples analyzed for DRO were or were not subjected to this cleanup procedures. In addition, all future analyses for DRO should be completed with and without the use of silica gel column cleanup in order to evaluate if non-target organic compounds of biogenic origin may be causing a positive bias.

Pg 5 –

11. In the Phase II investigation, DRO was reported as present in 28 of 35 samples were analyzed. The samples with the highest concentrations were PGMW01 at 638 ug/L from a 1:10 dilution, PGMW02 at 1,230 ug/L from a 1:10 dilution, PGMW03 at 62,100 ug/L from a 1:500 dilution, and PGMW04 at 4,830 ug/L from a 1:10 dilution. The chromatograms of these samples indicate a diesel-related fuel could possibly be present that elutes earlier than diesel #2, but can not be stated with certainty since other fuel products were not analyzed that could be used for comparison.

While a fuel product could be present in the samples listed above, DRO was also reported as detected in the associated field blank at 26.5 ug/L.

Therefore if these data were validated following guidance specified USEPA functional guidelines (U.S. EPA 2008), the results reported for PGMW01, PGMW02, and PGMW03 would be restated as undetected (U) because the concentrations prior to adjustment of the dilution factors were 15 times the concentration found in the field blank. The action limit would be $5 \times 26.5 \text{ ug/L} = 132.5 \text{ ug/L}$ and the concentrations prior to adjustment of the dilution factor would be 63.8 ug/L for PGMW01, 123 ug/L for PGMW02, and 124.2 ug/L for PGMW03

pg6

14. The report stated the detection of glycols in several domestic well samples analyzed using a GC/FID technique were likely reported as false positive (see page 27 of the report). The USEPA further stated these glycol detections could not be confirmed using a liquid chromatography with tandem mass spectroscopy analysis (note: referenced as GC/MS/MS in the report). Per USEPA interpretation of the initial reporting of false positive glycol results, the confirmatory nondetected results should be used for interpretative purposes and not the GC/FID results.

Notes: The USEPA report (see page 27) referenced the GC/FID technique used for the analysis of glycols as “EPA Standard Method 8015”, but should be SW-846 Method 8015D. The USEPA report (see page 27) used the acronym GC/MS/MS, which is the acronym for gas chromatography/mass spectrometry/mass spectrometry; however, the text stated liquid chromatography with tandem mass spectroscopy. This discrepancy should be corrected.

While the glycol analyses completed by HPLC/MS/MS during the Phase IV investigation were completed using a non-peer review method, the results of the quality control measurements are acceptable and these data are of generally good quality. These data tentatively indicate that glycol

target compounds are present in MW01 and MW02 and their presence should be confirmed using

other confirmatory techniques during future sample and analysis. In summary, results reported using this analytical technique should be used for interpretive purposes rather than the GC/FID results.

pg 7 –

15. The draft report states that some target compounds were present in associated blank water samples (e.g., method blanks, trip blanks, field blanks, and/or equipment rinse blanks). If the data were subjected to an appropriate degree of data validation, many results reported as detected

would be restated as undetected (U) because the concentrations found in the samples were !5 times (used for uncommon contaminants) or !10 times (used for common contaminants such as acetone for VOC analyses and phthalate compounds for SVOC analyses; see U.S. EPA) the concentrations found in the associated blanks. The affected results would then either be restated

as undetected (U) at the concentration found in the associated blank or at the concentration reported in the samples. Several examples of how blank contamination resulted in the reporting of

false positives for VOCs, GRO, and DRO were discussed above.

Ph 10 –

The USEPA states the detection of compounds associated with petroleum additives in groundwater would be “manifested as GRO, DRO, BTEX, naphthalenes, and trimethylbenzenes observed in deep monitoring wells.” Until all data have been subjected to a rigorous data verification and data validation review, this statement may not be factually correct.

Pg 11

The statement that trace levels of exotic organic compounds present in some samples may not be completely correct until a thorough data verification and validation review is completed.

Pg 12

USEPA noted in the SOPs listed below the following: “This Standard Operating Procedure has been prepared for the use of the Ground Water and Ecosystem Restoration Division (GWERD) of the U.S.

Environmental Protection Agency and may not be specifically applicable to the activities of other organizations. **THIS IS NOT AN OFFICIAL EPA APPROVED METHOD.** This document has not been through the Agency’s peer review process or ORD clearance process.”

The comment above is applicable to the following SOPs: handful of SOPs

While the SOPs listed above may be capable of generating acceptable data, the results reported may be

biased until they are subjected to a thorough technical review, are reproducible by commercial laboratories, and are officially approved.

Echelon Report dated March 27, 2012 (included with Papadopoulos

No QA Comments

Encana Letter dated April 18, 2012

No QA Comments

Undated four page list of questions

Case comments in lab report for TPH GRO/DRO says “some of the TPH/DRO chromatograms required manual integrations due to poor integration by the quantitation software. The quality of the data was improved by a more realistic Quantitation”. Please explain why the software would return a poor integration and what makes a quantitation more realistic.

How many samples collected from Phase 1-4 failed the EPA level 1 QA QC process and was this data removed from the dataset, flagged, or left in place with no notation?

Explain QA/QC requirements if one of the blanks (Field, trip, equipment, lab) were contaminated? One lab report seemed to flag a sample potentially influenced by a blank contamination, although many of the lab reports contained samples with contaminated blanks. If data from an actual sample is not significantly higher (10X) the concentration detected in one of blanks should that data be flagged in a lab report?